

# The crystal structure of cold compressed graphite

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(Dated: September 7, 2011)

Through a systematic structural search we found an allotrope of carbon with  $Cmmm$  symmetry which we predict to be more stable than graphite for pressures above 10 GPa. This material, which we refer to as Z-carbon, is formed by pure  $sp^3$  bonds and is the only carbon allotrope which provides an excellent match to unexplained features in experimental X-ray diffraction and Raman spectra of graphite under pressure. The transition from graphite to Z-carbon can occur through simple sliding and buckling of graphene sheets. Our calculations predict that Z-carbon is a transparent wide band gap semiconductor with a hardness comparable to diamond.

Thanks to the flexibility to form  $sp$ ,  $sp^2$  and  $sp^3$  bonds, carbon is one of the most versatile chemical elements. At ambient pressure, it is usually found as graphite (the most stable structure) or as diamond, but the richness of its phase diagram does not end there. In fact, many other structures have been proposed during the past years, especially since experimental data suggested the existence of a super hard phase of carbon. Evidences for a structural phase transition in compressed graphite to this unknown phase of carbon have been reported in numerous experiments [1–7]. In fact, in the range of 10 to 25 GPa one observes an increase of the resistivity [1] and of the optical transmittance [2, 3], a marked decrease of the optical reflectivity [4], changes in near  $k$ -edge spectra [7] and in X-ray diffraction (XRD) patterns [5–7]. Several hypothetical structures have been proposed to explain these features, such as hybrid  $sp^2$ – $sp^3$  diamond-graphite structures [8], M-carbon [9], bct- $C_4$ -carbon [10] and W-carbon [11]. However, none of these structures is able to match all experimental data in an unambiguous and fully satisfactory manner.

A common way to search for new crystal structures is to perform a systematic survey of the enthalpy surface using some sophisticated structure prediction method (for discussion on such methods see Ref. [12]). Here we use the minima hopping method [13] (MHM) for crystal structure prediction [14], which was designed to explore low-enthalpy phases of materials. This method was coupled to the all-electron projector-augmented wave method as implemented in the ABINIT code [15, 16]. Within the MHM, the system is moved from one configuration to the next by performing consecutive molecular dynamics escape steps and geometry relaxations. The

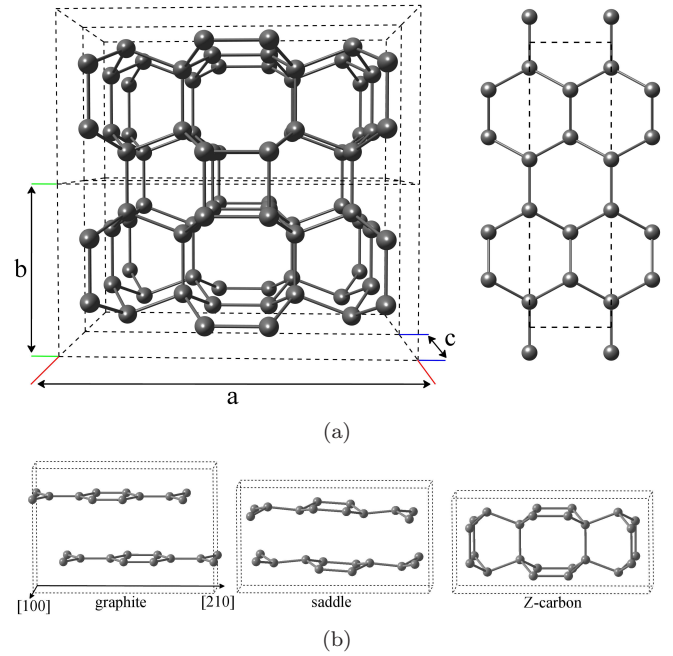


FIG. 1. (a) Structure of Z-carbon viewed from two different angles revealing planar four-membered and non-planar eight-membered rings forming chains along the  $b$ -direction and channels in the  $c$ -direction. The graphene sheets are in the  $a$ - $c$  plane. (b) Proposed transition pathway from graphite to Z-carbon.

initial velocities for the dynamics are aligned preferably along soft-mode directions in order to favor the escape to low enthalpy structures. Revisiting already known structures is avoided by a feedback mechanism. Relaxations are performed by the fast inertia relaxation engine [17]. The local density approximation was employed based on its good description of graphite. However, the enthalpy ordering was reconfirmed within the general-

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ized gradient approximation using two different functionals (PBE [18] and PBEsol [19]). The most promising candidate structures were then re-relaxed using norm conserving Hartwigsen-Goedecker-Hutter pseudopotentials [20]. Carefully converged Monkhorst-Pack  $k$ -point meshes were used together with a plane wave cut-off energy of 2100 eV.

The MHM was employed using simulation cells with 4 and 8 carbon atoms at a constant pressure of 15 GPa. We found, in addition to previously proposed structures of cold compressed graphite, a carbon phase that we call Z-carbon. This structure has  $Cmmm$  symmetry (see Fig. 1a) and, like diamond, is composed of  $sp^3$  bonds. The conventional unit cell has 16 atoms with cell parameters at 0 GPa of  $a = 8.668 \text{ \AA}$ ,  $b = 4.207 \text{ \AA}$ , and  $c = 2.486 \text{ \AA}$ , yielding a cell volume of  $V_0 = 90.7 \text{ \AA}^3$ . The two inequivalent carbon atoms occupy the  $8p$  and  $8q$  crystallographic sites with coordinates  $(1/3, y, 0)$  and  $(0.089, y, 1/2)$ , where  $y = 0.315$ . The structure contains four-, six- and eight-membered rings, where planar four-membered rings and non-planar eight-membered rings join together buckled graphene sheets. This structure can be interpreted as a combination of hexagonal diamond and bct- $C_4$ -carbon [21].

In contrast to other structure prediction methods like evolutionary algorithms or random search, the efficient escape moves in the MHM are based on fundamental physical processes. Therefore, minima found consecutively during a MHM simulation are usually connected through low enthalpy barriers. Since we have observed escape moves to and from Z-carbon to occur exclusively from and to graphite, we expect this transition to be the most probable. In Fig. 1b we show a possible transition pathway from graphite to Z-carbon. This process is a combination of sliding and buckling of the graphene sheets. The naturally staggered, i.e.  $AB$  stacked, graphene sheets slide along the  $[210]$  direction to an aligned  $AA$  stacking while the inter-layer distance decreases, and the aligned graphene sheets deform to create an alternating armchair-zigzag buckling.

In order to investigate the relative stability of Z-carbon, the calculated enthalpy difference with respect to graphite of several allotropes are compared in Fig. 2 as a function of pressure. Z-carbon has the lowest enthalpy among all proposed cold-compressed graphite phases, becoming more stable than graphite at 9.9 GPa (around 2.5 GPa below  $W$ -carbon).

We further investigated the dynamical lattice stability of this phase by computing the phonon dispersion in the whole Brillouin zone. We used linear-response theory in the framework of density functional perturbation theory [22] with the ABINIT code. A proper convergence was ensured with a  $12 \times 12 \times 12$   $k$ -point sampling, a  $4 \times 4 \times 4$   $q$ -point mesh, and a cut-off energy of 800 eV. All phonon modes were real confirming the structural stability of the structure. Furthermore, from a fit of the Murnaghan

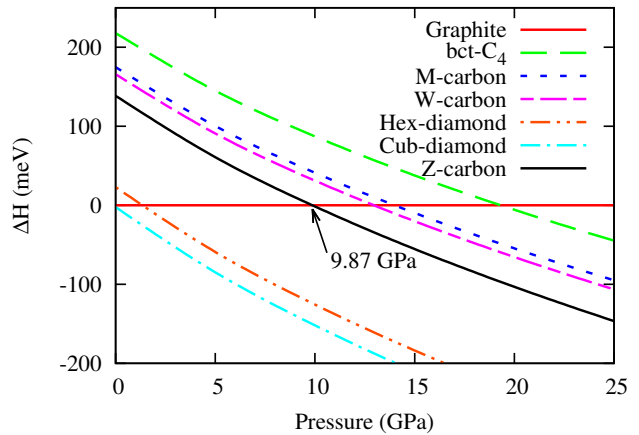


FIG. 2. Calculated enthalpy difference per atom with respect to graphite of several carbon allotropes as a function of pressure. Graphite is the horizontal line at zero. Z-carbon becomes more stable than graphite at around 10 GPa.

equation we obtained a bulk modulus of  $B_0 = 441.5 \text{ GPa}$ , and using the method proposed by Gao *et al.* [23] we calculated a Vicker's hardness of  $H_v = 95.4 \text{ GPa}$ . Both bulk modulus and hardness are extremely high and very close to the values for diamond ( $B_0^{\text{diamond}} = 463.0 \text{ GPa}$  and  $H_v^{\text{diamond}} = 97.8 \text{ GPa}$ ), which is compatible with the observed ring cracks in diamond anvil cells [7].

To investigate the energy gap of this material we used the perturbative many-body GW technique starting from the local density approximation [24]. These calculations reveal that Z-carbon is an indirect band-gap material with a gap of around 4.7 eV. Therefore, this material is expected to be optically transparent in agreement with experiments [2, 3].

We have gathered a considerable amount of experimental evidence that points to the presence of Z-carbon in cold compressed graphite samples. The first comes from the XRD experiment of Ref. [7]. In Fig. 3 we can see that the broadening of the XRD-spectra at high pressure can be explained by the coexistence of graphite and Z-carbon. However, the experimental curve can also be explained to some extent by the other proposed carbon allotropes [9–11] so that this experiment alone is not conclusive.

Other strong signatures for Z-carbon can be gathered from our measurements of Raman spectroscopy under pressure. These experiments were carried out at 300 K using the 514.5 nm line excitation of an  $\text{Ar}^+$  laser, and a Jobin-Yvon HR-800 Labram spectrometer with double-notch filtering with resolution better than  $2 \text{ cm}^{-1}$ . In the high pressure Raman measurements, we used a diamond anvil cell to apply pressure on two different samples (single crystals of graphite and highly oriented pyrolytic graphite), inside a 120 micron hole drilled in an iconel gasket. Argon and paraffin was used as the pres-

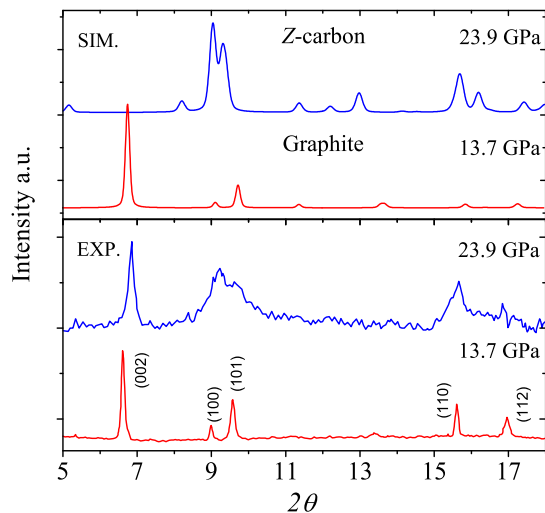


FIG. 3. Experimental XRD for cold compressed graphite at two different pressures from Ref. [7] and simulated XRD pattern for Z-Carbon (at 23.9 GPa) and Graphite (at 13.7 GPa). The main characteristics of the proposed carbon are perfectly in agreement with the experimentally observed changes.

sure medium. The pressure was determined by the ruby luminescence of a small chip ( $< 30$  microns). The laser was focused down to 3 microns with a power of about 20 mW on the sample.

The principal Raman active mode of graphite is the G-band at  $1579\text{ cm}^{-1}$  (at 0 GPa) which originates from the  $sp^2$  carbon atoms vibrating in-plane with  $E_{2g}$  symmetry. The effect of hydrostatic pressure on the linewidth of the G-band is shown in Fig. 4. The linewidth remains nearly constant until around 9–10 GPa. Above this value, the linewidth begins to broaden rapidly, in agreement with previous results of Hanfland *et al.* [3]. (A similar broadening has also been reported for turbostratic graphite-like  $BC_4$  under pressure [25].) This behavior is a sign of a structural transformation at this pressure, and can be explained by important changes in the Raman cross section caused by interlayer coupling and the formation of  $sp^3$  bonds. As seen in Fig. 2, Z-carbon becomes enthalpically favored with respect to graphite at around 10 GPa, whereas all other proposed structures cross the graphite line at significantly higher pressures.

Finally, we present the strongest direct evidence of the existence of Z-carbon, which is found in the Raman spectrum of graphite under hydrostatic pressure, shown in Fig. 5 for the energy range below the 1<sup>st</sup> order Raman peak of diamond ( $1332\text{ cm}^{-1}$  at 0 GPa) [26]. Neither graphite nor cubic-diamond have Raman active peaks in the selected energy region, however we can observe that a clear peak appears at  $1082\text{ cm}^{-1}$  for pressures higher than 9.8 GPa. This peak can not be explained by either bct-C4 carbon, M-carbon, nor by the pressure medium

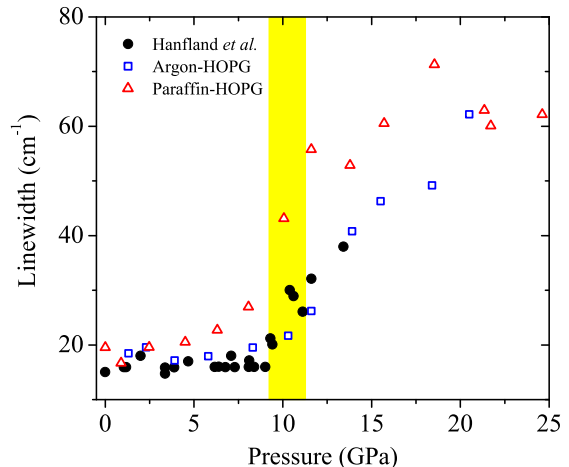


FIG. 4. Experimental linewidth of the G-band of graphite under pressure. The linewidth stays nearly constant until pressures of the order of 9–10 GPa, above which the linewidth begins to broaden rapidly. This is a strong evidence for a structural transition in graphite. Experiments were conducted using highly oriented pyrophillitic graphite (HOPG) and argon (squares) or paraffin oil (triangles) as pressure transmitting media. The black dots are taken from Ref. [3]

(argon). The only structures that have Raman active modes compatible with this experimental evidence are Z-carbon and W-carbon. For Z-carbon the frequencies are  $1096.5\text{ cm}^{-1}$  at 10 GPa and  $1110\text{ cm}^{-1}$  at 15 GPa. Incidentally, Z-carbon also has a Raman active  $A_g$  mode at  $1348.5\text{ cm}^{-1}$  at 0 GPa (theoretical value). This appears as a signature of planar four-membered rings that overlaps with the so-called defect D-band of graphite at around  $1345.5\text{ cm}^{-1}$  at 0 GPa (experimental value).

In conclusion, we identified an allotropic structure of carbon, Z-carbon, that becomes more stable than graphite above 10 GPa. From all known carbon allotropes, only cubic and hexagonal diamond have lower enthalpy at high pressures. The Z-carbon structure is as hard as diamond, and is transparent in the optical region. Moreover, a wide range of experimental data can only be explained by the presence of Z-carbon in samples of cold compressed graphite: first, the features of the X-ray diffraction spectra of graphite under pressure exhibit a broadening that matches the main peaks of Z-carbon. Second, the principal Raman signal of graphite, the G-band mode, suffers an abrupt increase of the linewidth above 9–10 GPa — the pressure range where Z-carbon becomes more stable than graphite. Third, a new peak at  $1082\text{ cm}^{-1}$  appears in the Raman spectrum of graphite at around 10 GPa, at the frequency of a Raman active mode of Z-carbon. The only candidate among all carbon allotropes proposed so far that can explain all above features simultaneously is Z-carbon.

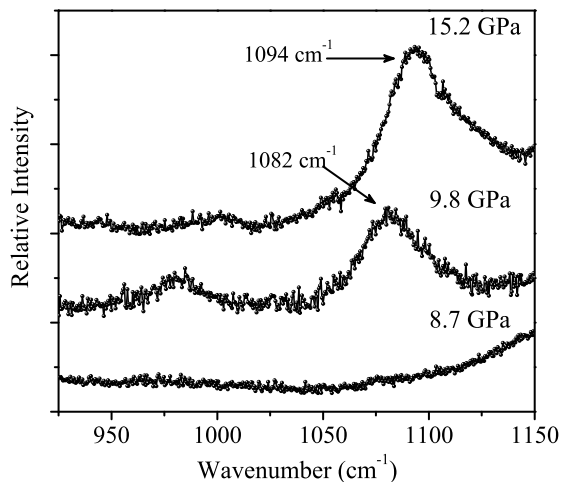


FIG. 5. Experimental Raman spectra of graphite under pressure. The peak around  $1082\text{ cm}^{-1}$  appearing at around 10 GPa and its evolution can be explained by either Z-carbon or W-carbon.

Our work also highlights the promising prospects of the minima hopping method for crystal structure prediction [14]. The exploration of the structural variety of even simple elements such as carbon was up to now typically the subject of many different studies which were presented in numerous papers over many years. In this first application of the MHM we were able to find not only Z-carbon, but also all other known carbon phases at the given pressure condition fully automatically. We can therefore expect that this method can also find with high reliability the low energy structures of many other materials for which our knowledge is at present still rudimentary, leading to important advances in the field of solid state physics.

We thank T. J. Lenosky and A. R. Oganov for valuable discussions. We thank Gilles Montagnac and Hervé Cardon, from the Laboratoire de Geologie de Lyon, France, for technical support during the Raman experiments. Financial support provided by the Swiss National Science Foundation is gratefully acknowledged. JAFL acknowledges the CONACyT-Mexico. SB acknowledges support from EUs 7th Framework Programme (e-I3 contract ETSF) and MALM from the French ANR (ANR-08-CEXC8-008-01). Computational resources were provided by the Swiss National Supercomputing Center (CSCS) in Manno and IDRIS-GENCI (project x2011096017) in France.

MA and JAFL contributed equally to this work.

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